

Advances in Electrochemical Nanoimprinting of Silicon: New Tooling and Stamp Materials

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Freeform 3D single-crystal inorganic semiconductor micro- and nano-structures offer the opportunity to design a myriad of optical devices such as metasurface-based elements¹. However, existing parallel bulk micromachining processes for semiconductors cannot fabricate 3D freeform and hierarchical micro and nanoscale 3D features². At the root of this challenge lies the indirect nature of existing parallel micromachining strategies that combine sacrificial templates such as gray-scale lithography with top-down processes such as deep reactive-ion etching to etch 3D structures³. Its indirect nature inherently produces poor out-of-plane patterning fidelity and resolution due to (a) poor mask selectivity, (b) scalloping effects, and (c) etch rate's dependence on feature size (**Error! Reference source not found.**a). Nanoimprinting lithography (NIL) was the first scalable processes to introduce nanopatterning of polymeric films with 3D freeforms and hierarchy. Since 2002, Chou et al proposed to extend NIL beyond polymers via thermal-NIL of polycrystalline silicon⁴. Despite a decade of efforts to extend NIL's library of patternable media, imprinting of inorganic single-crystalline semiconductors (e.g. Si) has not been plagued primarily due to recrystallization effects of heat-based approaches, generating area defects and condemning its optoelectronic properties. To resolve these challenges, this presentation explores wet-chemistry and catalysis⁵ to create a room-temperature etching-based technique to pattern semiconductors – known as metal-assisted chemical imprinting⁶ (Mac-Imprint) (**Error! Reference source not found.**b) - that selectively induces anisotropic etching at the contact points of the semiconductor-stamp interface (**Error! Reference source not found.**b). Particularly, novel mesoporous polymeric stamp materials coated in nanoporous gold and pressure-based immersion imprinting strategies are presented to overcome, respectively, mass-transport and contact non-uniformity limitations. Through engineering hierarchical meso and nanopores in the stamp, it becomes possible to approach within an order of magnitude the resolution limit of Mac-

¹N. Yu et al., "Designer spoof surface plasmon structures collimate terahertz laser beams," *Nature Materials*, 9, 2010.

²H. V. Jansen et al., "Black silicon method X [...]," *J. Micromech. Microeng.*, vol. 19 (033001), 2009.

³Y. Oppliger et al., "One-step 3D Shaping Using a Gray-Tone Mask for Optical and Microelectronic Applications," *Microelectronic Engineering*, 23(449), 1994.

⁴S. Y. Chou et al., "Ultrafast and direct imprint of nanostructures in silicon," *Nature*, 417(835), 2002.

⁵X. Li and P.W. Bohn, "Metal-assisted chemical etching in HF/H₂O₂ produces porous silicon," *APL*, vol. 77(2572), 2000.

⁶A. Sharstniou et al., "Electrochemical nanoimprinting of silicon," *PNAS*, 116 (21), 2019.

⁷B. Azeredo et al., "Direct Imprinting of Porous Silicon via Metal-Assisted Chemical Etching," *Advanced Functional Materials*, 26(17), pp. 2929, 2016.

Imprint as defined by the Debye length (1-2 nm) and reduce roughness to sub-10 nm levels.

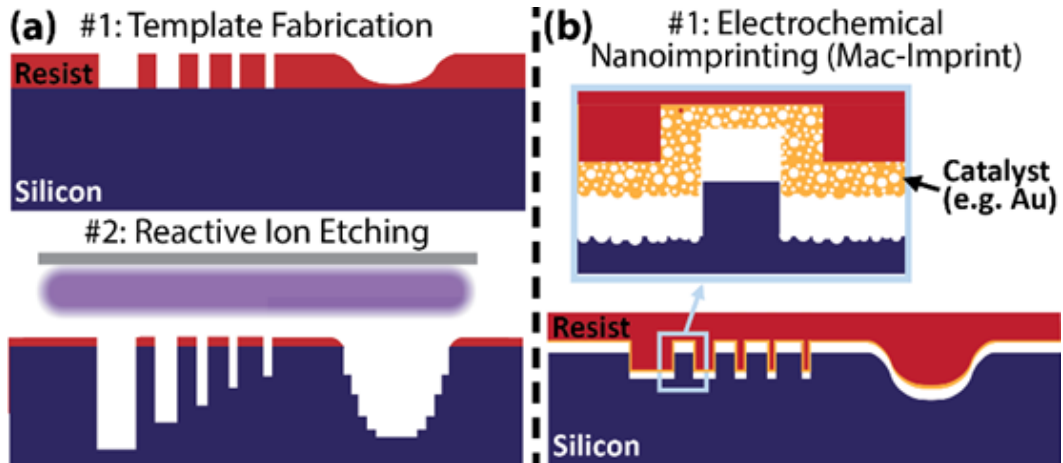


Figure 1: (a) Lithography combined with DRIE and its limitations in 3D patterning, and (b) advantages of Mac-Imprint.